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(54) Title: PURIFICATION OF PENTAFLUOROETHANE

(57) Abstract

A method for recovering essentially pure pentafluoroethane [HFC 125] from mixtures thereof with chloropentafluoroethane [CFC 115] comprising extractive distillation using an extractive agent selected from bromochloro-2,2,2-trifluoroethane and perfluorocarbons of 5 or more carbon atoms such as perfluoroalkanes and liquid perfluoropolyethers.

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PURIFICATION OF PENTAFLUOROETHANE

This invention relates to a process for the purification of pentafluoroethane (HFC 125) and particularly to a process for removing chloropentafluoroethane (CFC 115) from mixtures of HFC 125 and CFC 115 to provide essentially pure pentafluoroethane.

It has been proposed to manufacture HFC 125 by hydrogenation of CFC 115 in the gas phase at elevated temperature in the presence of a hydrogenation catalyst or by hydrofluorination of perchloroethylene or dichloro-1,1,1-trifluoroethane (HCFC 123) over a fluorination catalyst. These and other processes result in pentafluoroethane containing impurities and in particular CFC 115 which may be present in an amount of up to 20% or more and which needs to be removed from pentafluoroethane which is used as or as a component of refrigerant composition.

Removal of CFC 115 from HFC 125 is difficult owing to the closeness of the boiling points of the components and the azeotrope or azeotrope-like composition which forms between them which renders simple distillation impractical. At atmospheric pressure, CFC 115 boils at -38.7°C, HFC 125 at -48°C and the azeotrope at -55°C. At atmospheric pressure the azeotropic composition between HFC 125 and CFC 115 contains about 85 mole % of HFC 125 and 15 mole % of CFC 115 so that separation by azeotropic distillation at atmospheric pressure entails significant loss of HFC 125 per mole of CFC 115 removed from the mixture. At higher pressure the relative volatility of HFC 125 opposite CFC 115 is close to 1.0 as 100% purity of HFC 125 is approached so that separation by simple distillation is rendered impractical or indeed impossible.

It has been proposed in US 5,087,329 that CFC 115 can be removed from a mixture of HFC 125 and CFC 115 by a simple extractive distillation process using a fluorocarbon extractive agent having 1-4 carbon atoms and optionally containing hydrogen and/or chlorine atoms. The technique of extractive distillation is well known in the art and in respect of the HFC 125/CFC 115 mixture depends on the ability of the liquid extractive agent to selectively extract the CFC 115 from the mixture, thus increasing the relative volatility of HFC 125 opposite CFC 115 such that HFC 125 can be removed as a light fraction by simple distillation whilst the CFC 115 is retained in the liquid extractive agent. Essentially pure HFC 125 can be recovered in this way, for

example 99.8 or 99.9% purity as described in US 5,089,329. However, whilst the purity of the recovered HFC 125 may be excellent, the process described in US 5,087,329 suffers from the disadvantage that the extractive agents used are not sufficiently selective in respect of the extraction of CFC 115 and the recovery of HFC 125 in a single pass through the distillation column leaves something to be desired.

In theory, complete recovery of the HFC 125 by extractive distillation is possible by selecting an extractive agent which is 100% selective towards CFC 115 but this is virtually impossible in practice owing to the similar structures and properties of HFC 125 and CFC 115. The vast majority of potential extractive agents will absorb some HFC 125 as well CFC 115 and the best result that can be achieved is to minimise the amount of HFC 125 and maximise the amount of CFC 115 which are extracted from the mixture.

The present invention is based on the discovery of a class of extractive agents which exhibit an improved selectivity towards CFC 115 and thereby enable more efficient purification of HFC 125..

According to the present invention there is provided a method for purifying pentafluoroethane in a mixture containing pentafluoroethane and chloropentafluoroethane which comprises adding an extractive agent to said mixture, extractively distilling the mixture in an extractive distillation zone and recovering essentially pure pentafluoroethane from the extractive distillation zone, the extractive agent being selected from bromochloro - 2,2,2 - trifluoroethane (Fluothane) and perfluorocompounds of 5 or more carbon atoms.

The extractive agents used in the method according to the invention are selected on the basis of their ability to extract a relatively large proportion of CFC 115 compared to HFC 125 from the mixtures being treated. The extractive agents are bromochloro - 2,2,2 - trifluoroethane and perfluorocompounds of 5 or more carbon atoms. The perfluorocompound may be a perfluoroalkane such as perfluoropentane, perfluorohexane and perfluorodecalin in which the alkane is straight or branched chain and acyclic or cyclic or it may contain one or more atoms other than fluorine and carbon, for instance oxygen and may be for example a liquid perfluoropolyether. The

only limit on the number of carbon atoms in the compound is that the compound should be a liquid under the conditions of use as an extractive agent.

The method of the invention is broadly applicable to any mixture of HFC 125 and CFC 115 but is especially applicable to mixtures obtained in processes for the manufacture of HFC 125 by the reaction of hydrogen fluoride with C_2 compounds such as perchloroethylene and/or dichlorotrifluoroethane (HCFC 123) or chlorotetrafluoroethane (HCFC 124). The mixtures produced in such processes commonly contain appreciable proportions of CFC 115 for example up to 20% by weight. The mixtures may also be obtained by hydrogenation of CFC 115.

The method of the invention may be performed using conventional extractive distillation procedures. Thus, in a typical operation, a mixture containing HFC 125 and CFC 115 obtained as a reaction product in an HFC 125 production process is fed to the centre of a fractionating column whilst the liquid extractive agent is fed to the upper part of the column. As distillation proceeds, the gas phase rises up the column in countercurrent to the liquid phase which flows downwards through the column so that the column provides an overheads fraction comprising HFC 125 typically containing less than 100 ppm and sometimes less than 10 ppm by weight of CFC 115 and a bottom fraction comprising the extractive agent and CFC 115.

The column is suitably operated at a pressure of from 1 to 15 bar and a condenser temperature of from -50 to +45°C.

The extractive agent can be separated from the CFC 115 by conventional fractional distillation techniques and recovered for recycle to the extractive distillation column.

The invention will now be illustrated by reference to the accompanying drawing, the single Figure being a simplified flow diagram for the separation of HFC 125 from a mixture thereof with CFC 115.

Referring to the drawing, a distillation column 1 is provided with a feed line 2 to the centre of the column and a feed line 3 to the upper part of the column. An overheads flow line 4 leads from the top of the column 1 to a condenser 5. A product flow line 6 leads from the condenser 5 with a reflux flow line 7 leading from the product flow line 6 to the top of the column 1. A bottoms flow line 8 leads from the bottom of the

column 1 to a reboiler 9 with a vapour return line 10 leading from the top of the reboiler back to the bottom of the column. A flow line 11 leads from the reboiler 9.

In operation, a mixture containing HFC 125 and CFC 115 obtained from a fluorination reactor (not shown) is fed via line 2 to the column 1 which is maintained at a pressure of from 1 to 15 bar.

The liquid extractive agent is fed to the column 1 via line 3. As distillation proceeds an overheads fraction typically comprising HFC 125 containing less than 100 ppm by weight of CFC 115 is taken from the top of the column 1 via flow line 4, condenser 5 and flow line 6. A bottoms fraction comprising the extractive agent and CFC 115 is taken from the bottom of the column 1 via flow line 8, reboiler 9 and flow line 11.

The HFC 125 product obtained by the method of the invention may be subjected, as desired, to further purification procedures.

The invention is further illustrated but in no way limited by the following examples.

Examples 1 and 2

Vapour aliqouts of approximately 1 ml CFC 115 and 9 mls HFC 125 were added to an evacuated 100ml round-bottom flask fitted with a tap, a septum and a magnetic stirring bar. The flask was returned to atmospheric pressure by addition of air and an additional 18mls of air was added to create a slight positive pressure in the flask. A sample (5ml) of the vapours in the flask was removed and analysed by gas chromatography to determine the initial composition of the mixture of CFC 115 and /HFC 125. An extractant (10ml liquid phase) was added to the flask. The liquid was stirred for 1 hour and then a headspace sample (5ml) was removed for analysis by gas chromatography. Results are quoted in Table 1 below.

Table 1

Example No.	Extractant	Headspace Composition (mol%)	
		CFC 115	HFC 125
1	Initial Composition	12.4	87.6
	Fluothane[a]	9.1	90.0
2	Initial Composition	9.8	90.2
	Perfluoropentane[b]	6.4	93.6

a - averaged over 4 experiments

b - averaged over 2 experiments

In both examples the concentration of CFC 115 in the headspace is reduced after exposure to the extractant, indicating preferential solubility of CFC 115 in the liquid phase.

Examples 3 - 7

An evacuated 150ml flask fitted with tap, a septum and a magnetic stirrer was charged with known vapour volumes of CFC 115 of HFC 125 and let back up to atmospheric pressure. An additional 20 mls of air was added to generate a slight positive pressure in the flask. A 5ml vapour sample was removed and analysed by gas chromatography to determine the initial vapour concentration of the fluorocarbons. A known liquid volume of extraction agent (5-20mls) was added and the mixture was stirred at 0°C for 30 minutes after which a further 5ml sample was removed from the headspace and analysed by gas chromatography. The solubility of the fluorocarbon (and the partial pressure of fluorocarbon at equilibrium) was calculated from the difference in the initial vapour concentration of the fluorocarbon and the concentration in the headspace after equilibration.

The results are summarised in Table 2 below, where α is the ratio of the concentration of dissolved CFC 115: concentration of dissolved HFC 125 in the liquid phase at an equilibrium partial pressure of 0.4 atmospheres of fluorocarbon.

Table 2

Example	Extractant	α	Solubility of CFC 115	Solubility of HFC 125
3	Perfluorodecalin	2.4	0.82a	0.34a
4	Perfluorohexane	2.1	0.82a	0.39a
5	Perfluoropentane	1.9	0.97a	0.52a
6	Galden HT 200*	2.1	0.8b	0.38b
7	Fomblin Z15*	3.3	0.62b	0.19b

a - Solubility expressed in Mole Fraction x 10^{-2}

b - Solubility expressed as [Moles CFC 115 or HFC 125] ÷ [wt in gm of Perfluoropolyether x10^{-4}]

* Galden and Fomblin fluids are perfluoropolyethers supplied by Ausimont Spa. Galden HT 200 has an average molecular weight of 870. Fomblin Z15 has an average molecular weight of 4000.

Comparative Expamples

For purposes of comparison the above procedure was repeated twice using extractants outside the scope of the invention.

The results as shown in Table 3

Table 3

Example No	Extractant	α	Solubility of CFC 115	Solubility of HFC 125
1	HCFC 123	1.3	5.2	4.1
2	n-Pentane	1.4	2.8	2

Solubilities are in mole fraction x 10^{-2}.

HCFC 123 is 1,2-dichloro-1,1,2-trifluoroethane

A comparison of the " α " results in Table 2 with those in Table 3 shows that the extraction agents used in Table 2 are more selective towards CFC 115 than the agents used in Table 3.

CLAIMS:

1. A method for purifying pentafluoroethane in a mixture containing pentafluoroethane and chloropentafluoroethane which comprises adding an extractive agent to said mixture, extractively distilling the mixture in an extractive distillation zone and recovering essentially pure pentafluoroethane from the extractive distillation zone, wherein the extractive agent is selected from bromochloro-2,2,2-trifluoroethane and perfluorocompounds of 5 or more carbon atoms.

2. A method as claimed in claim 1 wherein the extractive agent is bromochloro-2,2,2-trifluoroethane or perfluoropentane.

3. A method as claimed in claim 1 or claim 2 wherein the mixture and the extractive agent are passed in countercurrent through the extractive distillation zone.

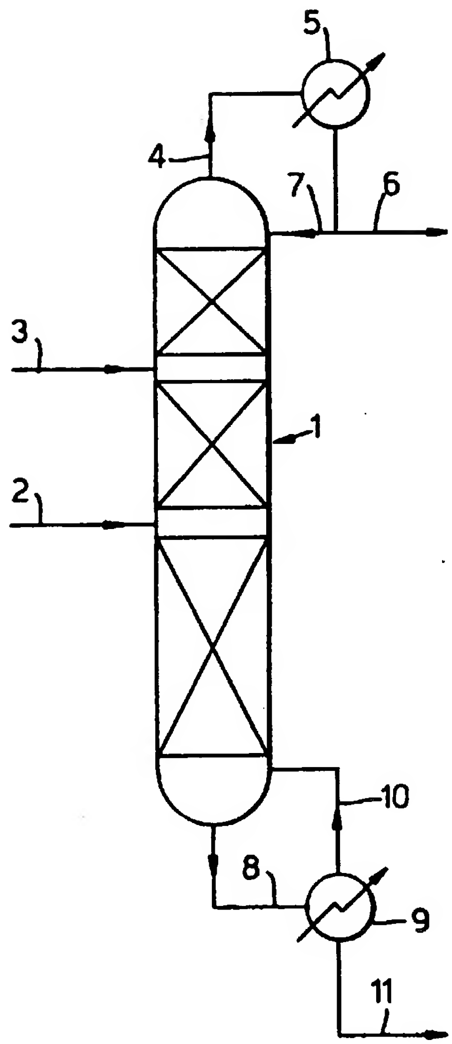
4. A method as claimed in claim 1, 2 or 3 wherein the extractive distillation is effected at a pressure of from 1 bar to 15 bar.

5. A method as claimed in any one of claims 1 to 4 wherein the extractive distillation is effected at a condenser temperature of from -50°C to +45°C.

6. A method as claimed in any one of the preceding claims wherein the extractive agent containing chloropentafluoroethane is distilled to recover the extraction agent which is recycled to the extractive distillation zone.

7. A method as claimed in any one of claims 1 and 3 to 6 wherein the extractive agent is a perfluoroalkane.

8. A method as claimed in any one of claims 1 and 3 to 6 wherein the extractive agent is a perfluoropolyether.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INTERNATIONAL SEARCH REPORT

Intern. nal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C17/386 C07C19/08 C07C19/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 087 329 (V.M. FELIX) 11 February 1992 cited in the application see the whole document -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. .onal Application No
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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